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Silver halide color photographic light-sensitive material (54)

A silver halide color photographic light-sensitive material comprising a support and provided thereon, a blue-sensitive, a green-sensitive and a red-sensitive silver halide emulsion layer, wherein at least one of said red-sensitive silver halide emulsion layer comprises at least one compound represented by Formula 1 or Formula 2:

## Formula 1

## Formula 2

wherein  $R_1$  and  $R_2$  independently, and  $R_1$  and  $R_2$  independently represent an aliphatic group, provided that the total number of carbon atoms contained in R1 and R2 and in Q1 and Q2 is 8 or more, R3 and Q3 independently represent a substituent; n and m are each 0 or 1 and R and Q independently an aliphatic group, and aryl group or a heterocyclic group.

### Description

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#### Field of the invention

This invention relates to a cyan dye-forming coupler and, more specifically, to a silver halide light-sensitive color photographic material, which contains a 1-naphthot-type cyan dye-forming coupler having in its second-position an orthotographic material position and photographic material position and photographic part of the discontinuous productions of the discontinuous disc

## Background of the invention

Heretotore, a color image is formed by imagewise exposing a silver halide light-sensitive color photographic material and undergring color development in which a dye image is formed by the reaction of a dye-forming coupler with a paraphenylenediamine-type color developing agent.

In this photographic process, color reproduction by subtractive color system is generally employed and yellow, magenta and cyan dye images are produced.

As for cyan dye-forming coupler, phenol type and naphthol type compounds are representative and, among them, naphthol-type compounds are used in color negative littles for their photographic characteristics showing sufficient light absorption in the long wavelength region and high coupling reactivity.

Heretofore, naphthol type compounds, of which second-position is substituted by a carbamoyl group have been used. However, there has been a problem that color density tends to be reduced when this type of cyan dye is processed with a fatiqued blaces boultune.

On the other hand, 2-arylcarbemoyl-1-naphthol-type couplers disclosed in U.S. Patent No.3,488,193, have an advantage that color density is not tend to decrease when processed with a fatigued bleaching solution, however, they have disadvantages that the maximum absorption wavelength shifts to short wavelength side in high color density area and color peroduction property is poor.

For the purpose of improving the above-mentioned disedvantages, 2-anylcarbamoyl-1-naphthol type cyan couplers disclosed in Japanese Patent Publication No.82-93747 (1987), have an advantage that the maximum absorption were length dose not shift mentarisally to short wevelength side, however, the cyan couplers have a disadvantage that, in conventional color nega type developing, the maximum absorption wavelength becomes often the wavelength of not less than 700m. A preferable wavelength range is within the range of 655m to 700m, so that the maximum avelength is longer than the preferable wavelength and color reproduction is poor. Recently, although there have been a demand for a silver halide color photographic material harvith pigh sensitivity, the color forming property of the above-mentioned for a silver halide color photographic material harvith pigh sensitivity, the color forming property of the above-mentioned for a silver halide color photographic material harvith pigh sensitivity, the color forming property of the above-mentioned for a silver halide color photographic material harvith pigh sensitivity, the color forming property of the above-mentioned for a silver halide color photographic material harviter to the strength of the silver of the silver

# Summary of the Invention

The first object of the present invention is to provide a silver halide color photographic light-sensitive metorial, which is capable of producing a dye image of enhanced sensitivity and improved image quality by employing a 1-naphthol-type cyan dye-forming coupler.

The second object of the present invention is to provide a silver halide color photographic light-sensitive material comprising a 1-nephtho-type cyan dye-loming coupler which is capable of torming a yard dye image having a favorable spectral absorption property and, especially having a favorable maximum absorption wavelength

The third delect of the present invention is to provide a silver halide color photographic light-sensitive material which comprises a 1-naphthotype cyan dye-forming coupler where the density loss of the cyan dye produced therefrom is reduced even when it is processed with a failigue

The fourth object of the present invention is to provide a silver halide light-sensitive color photographic material having improved storage stability before exposure.

The above-mentioned objects of the present invention have been attained by the following items.

Item 1: A sliver halide color photographic light-sensitive material comprising a support and provided thereon, a blue-sensitive sliver halide emulsion layer, a green-sensitive sliver halide emulsion layer and a red-sensitive sliver halide emulsion layer, wherein said red-sensitive sliver halide emulsion layer comprises a compound represented by Formula 1 or Formula 2:

## Formula 1

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wherein R<sub>1</sub> and R<sub>2</sub> independently represent an aliphatic group, provided that the total number of carbon atoms contained in R<sub>1</sub> and R<sub>2</sub> is 8 or more; R<sub>2</sub> represents a substituent; n is 0 or 1 and R represents an aliphatic group, an any group or a hetercoyclic group;

## Formula 2

$$\begin{array}{c} OH \\ OQ_1 \\ |_{=} Q_2 \\ (Q_3)_m \end{array}$$

wherein  $\Omega_1$  and  $\Omega_2$  independently represent an aliphatic group, provided that the total number of carbon atoms contained in  $\Omega_1$  and  $\Omega_2$  is 8 or more;  $\Omega_2$  represents a substituent; m represents 0 or 1;  $\Omega$  represents an aliphatic group, an any floroup or a heterocyclic group.

Item 2: The silver halide color photographic light-sensitive material of item 1, wherein said red-sensitive silver halide emulsion layer further comprises a compound represented by Formula 6:

### Formula 6

$$R_{12}CONH \xrightarrow{OH} NHCONHR_{11}$$

wherein  $R_{11}$  represents an anyl group or a heterocyclic group;  $R_{12}$  represents an alkyl group or an anyl group, provided that  $R_{12}$  may form a group capable of forming a dimer or an oligomer with  $R_{11}$  or  $R_{12}$ :  $X_{11}$  represents a hydrogen atom or a group capable of splitting off upon reaction with an oxidation product of a color developing agent.

Item 3: The silver halide color photographic light-sensitive material of item 1, wherein said red-sensitive silver halide emulsion layer further comprises a compound represented by Formula A-1:

# Formula A-1

$$_{R_{21}CON} {\scriptsize < \atop \begin{array}{c} R_{22} \\ R_{23} \end{array}}$$

wherein  $R_{21}$ ,  $R_{22}$  and  $R_{23}$  independently represent a hydrogen atom, an alkyl group, a cycloalkyl group or an aryl group.

Item 4: The silver halide color photographic light-sensitive material of item 1, wherein said -O-Q of said Formula 2 represents an aliphaticoxy group, a heterocyclicoxy group or a

wherein P<sub>A</sub> represents an alkyl group, a nitro group, an amino group, an alkoxyl group, a hydroxyalkyl group, a asylsmino group, a carboxyl group, a asylsmino group, an anylsmino group, an alkylsmino group, an alkylsmino group, an alkylsmino anylsmino group, an alkylsmino group, an alkylsmino group, an alkoxyl group, an alkoxyl group, an alkoxyl group, an alkylsmino group, an anylsmino group, a nitro group, a deplanino group, a carboxyl group, an alkylsmino group, an anylsmino group, and anylsmino group, an anylsmino group, an anylsmino group, and anylsmino group, an anylsmino group, an anylsmino group, and anylsmino group, and anylsmino group, an anylsmino group, and anylsmin

Item 5: The silver halide color photographic light-sensitive material of item 1, wherein the compound represented by said Formula 1 is represented by Formula 3:

# Formula 3

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wherein R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub> and R<sub>7</sub> independently represent a straight-chained or branched alkyl group, provided that the total number of carbon atoms contained in R<sub>4</sub> through R<sub>7</sub>, is 6 through 28; R' represents a substituted alkyl group haying 2 (5 30 carbon atoms or a substituted phyl group haying 6 to 30 carbon atoms.

Item 6: The silver halide color photographic light-sensitive material of item 1, wherein the compound represented by Formula 2 is represented by Formula 4:

# Formula 4

wherein Q<sub>4</sub> represents a straight-chain, branched or cyclic allyl group; Q<sub>6</sub> represents a tertiary allyl group, where 4 to 20 carbon atome or a five member or six-member cyclic allyl group; Q'impresents a substituted allyl group having 2 to 30 carbon atoms or a substituted plenyl group having 6 to 30 carbon atoms.

Item 7: The silver halide color photographic light-sensitive material of item 6, wherein said -O-Q' of said Formula 4 represents an aliphaticoxy group, a heterocyclicoxy group or a

$$-0$$
 $(NHCO)_n - R_B$ 
 $(R_A)_-$ 

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wherein PA, represents an alkyl group, a nitro group, an amino group, an alikoxyl group, a hydroxyalkyl goup, a carboxyl group, an ankylsulforyl group, an anylsulfyl group, an alkylsulforyl group, an anylsulforyl group, and anylsulforyl group, and

Item 8: The silver halide color photographic light-sensitive material of item 2, wherein the compound represented by Formula 1 or Formula 2 and the compound represented by Formula 6 are contained in a molar ratio of 1:1 to 1:10.

Item 9. The silver halide color photographic light-sensitive material of item 1, wherein said compound represented by Formula 1 or Formula 2 is contained in an amount of  $1\times 10^{-3}$  mol to  $8\times 10^{-1}$ mol per mol of silver halide.

Item 10: The silver halide color photographic light-sensitive material of item 1, wherein said compound represented by Formula 1 or Formula 2 is contained in an amount of  $1 \times 10^{-2}$  mol to  $8 \times 10^{-1}$ mol per mol of sliver halide.

Herein below, the cyan dye-forming coupler represented by Formula 1 will be described in detail.

As for the aliphatic group represented by R<sub>1</sub> and R<sub>2</sub>, straight-chained, branched or cyclic alkyl group, an alkenyl group and an alkynyl group, which may have a substituent, can be mentioned.

The aliphatic group represented by Fl includes preferably, those having 4 to 20 carbon atom such as, for example, butyl group, iso-butyl group, pentyl group, neo-pentyl group, iso-butyl group, cyclohaxyl group, cotyl group, 2-2-tylyhaxyl group, decyl group, 2-betylodyl group, 2-betylodyl group, 2-hexyldeoyl group, 2-betylodyl group, 2

The aliphic group represented by  $P_B$  includes preferably an alkyl group having 1-20 carbon atoms such as, for example, methyl group, ethyl group, propyl group, iso-propyl group and those mentioned concerning R<sub>1</sub>. The total number of carbon atoms contained in R<sub>1</sub> and R<sub>2</sub> is 8 or more, and it is preferably to 10 to 32 and, more preferably, at least one of them is a branched alkyl group.

R<sub>3</sub> represents a substituent including, for example, an aliphatic group, an anyl group, a halogen atom, a hydroxyl group, an amino group, a carbonamide group, a sulfonamido group, a unido group, an acyloxy group, an aliphaticoxy group, and a sulfamoylamino group.

As for the aliphatic group represented by R in Formula 1, a straight-chained, branched or cyclic alikyl group having 1 to 30 carbon atoms and a substituted alikyl group have preferable and, a substituted alikyl group having 2 to 50 carbon atoms is more preferable. As for the substituted alikyl group, it or sample, a carbonyl group, an aliphaticoxy group, a substituted and group, a fallong atom, a urelian group, a nacylony group, a cabamoyloxy group, a hydroxyl group, an anyl-group, a nacylony group, an aning group, an arelian gro

As for the aryl group for IT, substituted or unsubstituted phenyl or naphthyl group is preferable. And, a substituted phenyl group having 6 to 30 carbon atoms is especially preferable. As for the substituted of the substituted phenyl group, for example, those groups mentioned as the substituted for the substituted alkyl group for IT can be mentioned.

As for the heterocyclic group for R, a five-member or six-member heterocyclic ring containing therein at least one hetero atom selected from hitrogen, oxygen and sulfur, or a fused ring formed from the above-mentioned five-member or six-member heterocyclic ring and another aromatic ring or a heterocyclic ring is preferable, and these fused rings may be substituted by a proper substituent, such as those mentioned as the substituent for the substituted alkyl group recreasered by R.

As R, an aliphatic group or an aryl group is preferable. Among compounds represented by Formula(I), especially preferable compound can be presented by Formula 3.

## Formula 3

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$$\begin{array}{c} \text{OCH}_2\text{CH} < \stackrel{R_4}{R_5} \\ \text{OCH}_2\text{CH} < \stackrel{R_6}{R_7} \end{array}$$

wherein R4, R5, R6 and R7 independently represent a straight-chained or branched alkyl group, provided that the total number of carbon atoms contained in R4 through R6 is 6 through 28; R' represents a substituted alkyl group having 2 to 30 carbon atoms or a substituted phenyl group having 6 to 30 carbon atoms.

As for the example of the substituent for the substituted alkyl group or the substituted phenyl group represented by RI, those groups mentioned as the examples of the substituent for the substituted alkyl group in the aliphatic group as R can be mentioned.

Next, the cvan dye-forming coupler represented by Formula 2 is described in detail:

The aliphatic group represented by Q1 and Q2, is straight-chained, branched or cyclic alkyl, alkenyl or alkynyl group, and the aliphatic group may have a substituent. As for the aliphatic group represented by Q1, an alkyl group having 4 to 20 carbon atoms, is preferable, and the alkyl group preferable includes, for example, butyl group, iso-butyl group, pentyl group, neo-pentyl group, iso-pentyl group, hexyl group cyclohexyl group, octyl group, 2-ethylhexyl group, decyl group, dodecyl group, 2-methyloctyl group, 2-butyloctyl group, 2-hexyldecyl group, 5,7-di-methyloctyl group, 3,5,5-trimethylhexyl group and hexadecyl group. As for the aliphatic group represented by Q2, an alkyl group having 2 to 20 carbon atoms is preferable and, more preferably, a branched or a cyclic alkyl group having 4 to 20 carbon atoms, including, for example, sec-butyl group, tert-butyl group, 1,1,3,3-tetramethylbutyl group, cyclopentyl group, cyclohexyl group, 1-ethyl-1-methylpropyl group, 1-ethyl-1-methylpentyl group, 1-hexyl-1-methylnonyl group, bicyclooctyl group, admantyl group. The total number of carbon atoms contained in Q1 and Q2 is 8 or more, and it is preferably to 10 to 32.

Q<sub>3</sub> represents a substituent, and a substituent preferable includes, for example, an aliphatic group, an aryl group, a halogen atom, a hydroxyl group, an amino group, a carbonamide group, a sulfonamido group, a ureldo group, an acyloxy group, an aliphatic oxy group, an aliphatic thio group, an aryl thio group and a sulfamoylamino group.

As for the aliphatic group represented by Q in Formula 2, a straight-chained, branched or cyclicalkyl group having 1 to 30 carbon atoms and a substituted alkyl group are preferable and, especially, a substituted alkyl group having 2 to 30 carbon atoms is preferable. As for the substituent for the substituted alkyl group, for example, a carboxyl group, an allphaticoxycarbonyl group, an aliphaticoxy group, an aryloxy group, an aliphaticthio group, an arylthio group, a sulfonyl group, an acyl group, a carbamoyl group, a sulfamoyl group, an acylamino group, a sulfonamido group, a halogen atom, a ureido group, a urethane group, an acyloxy group, a cabarnoyloxy group, a hydroxyl group, an aryl group, a heterocyclic group, a cyano group, a nitro group, an arnino group, an oxalyl group and an oxamide group can be mentloned.

As for the anyl group for Q, substituted or unsubstituted phenyl or naphthyl group is preferable. And, a substituted phenyl group having 6 to 30 carbon atoms is especially preferable. As for the substituent of the substituted phenyl group, for example, those groups mentioned as the substituent for the substituted alkyl group for Q can be mentioned,

As for the heterocyclic group for Q, a five-member or six-member heterocyclic ring having therein at least one hetero atom selected from nitrogen, oxygen and sulfur, or a fused ring formed from the five-member or six-member heterocyclic ring and another aromatic ring or a heterocyclic ring is preferable, and these fused rings may be substituted by a substituent, such as those mentioned as the substituent for the substituted alkyl group represented by Q.

As Q, an aliphatic group or an aryl group is more preferable.

Among compounds represented by Formula 2, especially preferable example, one represented by Formula 4 can be mentioned:

#### Formula 4:

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wherein C<sub>4</sub> represents a straight-hain, branched or cyclicalityl group such as those mentionad above as the group, 1.1,3-5 trained by C<sub>4</sub> C<sub>7</sub> represents a tertiary allyl group having 4 to 20 carbon atoms such as tert-butyl group, tart-smyl group, 1.1,3-5 trained mylloyling topun, 1-attyl-1-methylpentyl group, 1-hayt-1-methylnonyl group, bloyclocctyl group and adamantyl group or a five member or six-member cyclicalityl group such as cyclichonyl group; C' represents a substituted allyl group having 5 to 30 carbon atoms or a substituted phonyl group having 6 to 30 carbon atoms.

As for the examples of the substituent for the substituted alkyl group or the substituted phenyl group represented by C!, those groups mentioned above as the substituent for the substituted alkyl group in the allphatic group represented by Q in Formula 2 can be mentioned.

Hereunder, compounds represented by the above-mentioned Formulae 6 and A-1 will be described in detail.

As for the any igroup represented by R<sub>11</sub> or R<sub>12</sub>, for example, a phenyl group and a nainthly group can be mentioned. As for the substituent for the groups erpresented by R<sub>11</sub> or R<sub>12</sub>, for example, a hatopen atom, a nitring group, a consequence of the property of the group of the group, an any or group, an allow group, a carbonny group, a sufferony group, an allow group, a carbonny group, a sufferony group, an allow group, a carbonny group, a sufferony group, an allow group, an allow group, a carbonny group group, a sufferony group, an allow group, a carbonniant group and sufferont group carbon mentioned.

Preferable number of the substituent is preferable to be 1 to 5, provided that when there are two or more of substituents, they may be either same or different.

Preferable substituent on R<sub>11</sub> are a halogen atom, an alkylsulfonyl group and a cyano group.

Preferable group as R<sub>12</sub> is one represented by Formula B;

Formula B 
$$(R_{14})_{\,K} \qquad (J-R_{13})_{\,L}$$

wherein, J represents an oxygen atom or a sulfur atom; k represents an integer of 0 to 4; 1 represents zero or one, provided that when k is two or more, the plural number of  $R_{14}$ , may be either seme or different,  $R_{13}$  represents a alloylane group,  $R_{14}$ , represents a substituent. As for the substituent represented by  $R_{14}$  for example, an alkyl group, an aryloxy group, an alkoxy group, an aryloxy group, an a

group, an acystemin group; a sunchainted group; a cataland group group and a manyloxy group, a carbamoyloxy group, As for the elimination group represented X<sub>1</sub>, for example, a halogen atom, an anyloxy group, a carbamoyloxy group, a carbamoyloxy group, as sulfonamido group and a succinicimido group can be mentioned.

As for the more specific examples, those disclosed in U.S. Patent Nos. 3, 476, 563 and 3,749,735, Japanese Patent Publication O.P.I. Publication No. 47-37426(1972), Japanese Patent Publication No. 49-36934(1973), Japanese Patent O.P.I. Publication No. 50-10136(1975), 50-117422(1975), 50-130441(1975), 51-108841(1976), 50-120334(1975), 52-13015(1977) and 53-105226(1978), can be meritioned.

R<sub>21</sub>, R<sub>22</sub> and R<sub>23</sub> independently represent a hydrogen atom, an alkyl group, a cycloalkyl group or an anyl group and, among these groups, the alkyl group is preferable.

Those groups mentioned above may have a substituent and such substituent includes, for example, an allyl group, a cyclosility group, an altenyl group, an any group, an explaining group, a sulforamido group, an allylithin group, an appliting group, a hategony atom, a heterocyclic group, a sulforal group, a phosphoryl group, an apply group, a phosphoryl group, an apply group, a laterocyclicoxy group, a carbamoyl group, a sulfamoyl group, a carbamoyl group, an apply group, a carbamoyl group, an apply group, a carbamoyl group, an alteny group, a carbamoyl group, an alteny group, an alteny group, a carbamoyl group, an alteny group, an alteny group, an alteny group, an alteny group and proper group and group group group and group grou

Herein below, specific examples represented by Formulae 1 and 2 are shown:

General Formula (1)

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(R<sub>3</sub>)<sub>n</sub>

	ĸ	NHCOCH <sub>2</sub> CH <sub>2</sub> COOH	-CH2CONHCH2CH2OCH3	-NHCOCH C <sub>2</sub> H <sub>9</sub>	-CH2COOCH3	-сн2соон	-NHCOCH <sub>2</sub> CHCOOH
	뙶	1		1	1	,	,
į	ជ	0	0	0	0	0	0
	R2 .	5-CH <sub>2</sub> CH <sub>2</sub> C <sub>2</sub> H <sub>3</sub>	5-CH <sub>2</sub> CH <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	5-CH <sub>2</sub> CH <sup>-</sup> C <sub>2</sub> H <sub>5</sub>	5-CH <sub>2</sub> CH C <sub>2</sub> H <sub>5</sub>	5-CH <sub>2</sub> CH <sup>-</sup> C <sub>2</sub> H <sub>5</sub>	5-CH <sub>2</sub> CH C <sub>2</sub> H <sub>5</sub>
	R1	-CH2CH C2H5	-CH <sub>2</sub> CH C <sub>2</sub> H <sub>5</sub>	-CH <sub>2</sub> CH C <sub>2</sub> H <sub>9</sub> 5	$-\mathrm{CH_2CH} \stackrel{\mathrm{C_4H_9}}{\sim} \mathrm{C_2H_5}$	-CH <sub>2</sub> CH C <sub>2</sub> H <sub>5</sub>	-CH <sub>2</sub> CH C4H <sub>9</sub>
	Compound No.	I-1	1-2	I-3	1-4	I-5	1-6

R <sub>1</sub> R <sub>2</sub> n R <sub>3</sub> R	С. С	C <sub>2</sub> H <sub>2</sub> S-CH <sub>2</sub> CH C <sub>2</sub> H <sub>3</sub> 0 - CHCOOH C <sub>2</sub> H <sub>3</sub> C <sub>2</sub> H <sub>3</sub> C <sub>2</sub> H <sub>3</sub> C <sub>2</sub> H <sub>3</sub> S	5-CH <sub>2</sub> CH <sub>5</sub> 0 -	$\begin{pmatrix} C_4H_9 \\ C_2H_5 \end{pmatrix} = 5 - CH_2CH \\ C_3H_5 \end{pmatrix} = \begin{pmatrix} C_{13} \\ C_{13} \end{pmatrix} = 0$	$\begin{pmatrix} CH_3 \\ CH_3 \end{pmatrix}$ S-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> $\begin{pmatrix} C_4H_9 \\ C_2H_3 \end{pmatrix}$ 0 - $\begin{pmatrix} C_{11} \\ C_{22} \end{pmatrix}$	S-CH <sub>2</sub> CH C <sub>6</sub> H <sub>13</sub> 0 -	5-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> 0 - CHCOOH C <sub>12</sub> H <sub>25</sub>		$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Celtis 5-Chach
R <sub>1</sub>	-CH2CH C2H5 5-CI	-CH <sub>2</sub> CH C <sub>2</sub> H <sub>5</sub> 5-CI	-CH2CH C4H9 5-CI	-CH <sub>2</sub> CH <sub>2</sub> 5-C	1			-CH2CH CH3 5-C	-CH2CH CH3 5-C	_
Compound	I-7	I-8	6-1	I-10	1-11	1-12	1-13	į-14	I-15	1-16

I-17 -CH <sub>2</sub> C	Ľ.	R2	п	R3	Я
	-CH2CH C4H3	5-CH <sub>2</sub> CH C4H <sub>9</sub>	0	_	MHCOCH <sub>3</sub>
	-CH <sub>2</sub> CH C <sub>6</sub> H <sub>13</sub>	5-CH <sub>2</sub> CH CH <sub>3</sub>	•	-	-CH2CH2C1
I-19 -CH <sub>2</sub> C	$-\text{CH}_2\text{CH} \begin{array}{c} \text{C}_8\text{H}_{17} \\ \text{C}_6\text{H}_{13} \end{array}$	5-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	0	١.	-CH2COOC12H25
I-20 -CH <sub>2</sub> C	-CH2CH C6H17	$5$ -CH <sub>2</sub> CH $^{\prime}$ C <sub>6</sub> H <sub>13</sub>	0	-	——————————————————————————————————————
I-21 -CH <sub>2</sub> C	-CH2CH CH3	5-(n)C <sub>12</sub> H <sub>2</sub> 5	0	ı	-снсоос <sub>3</sub> н <sub>7</sub>   сн <sub>3</sub>
I-22 -(n)(	-(n)C <sub>12</sub> H <sub>25</sub>	5-CH <sub>2</sub> CH CH <sub>3</sub>	0	1	- NHCOOC <sub>2</sub> H <sub>5</sub>
I-23 -CH <sub>2</sub> C	-CH <sub>2</sub> CH C <sub>6</sub> H <sub>17</sub>	5-сн <sub>3</sub>	0	1	-CH2CH2CN
I-24 -CH <sub>2</sub> C		$^4$ -CH <sub>2</sub> CH $^{\prime}$ C <sub>2</sub> H <sub>5</sub>	0	ı	- NHSO <sub>2</sub> CH <sub>3</sub>
· 1-25 -CH <sub>2</sub> C	-CH2CH C2H5	6-CH <sub>2</sub> CH C <sub>2</sub> H <sub>5</sub>	0	1	$- \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$
I-26 -CH <sub>2</sub> C	-CH2CH C2H5	$6\text{-CH}_2\text{CH}_1 \atop \text{C}_6\text{H}_{13}$	0		-СН2СН2SCH2COOH

# EP 0 690 344 A1

Compound No.	R1	R2	n	R3	т.
_	-CH2CH C2H5	$C_{SH_{11}}(t)$ 6- $CH_{2}CH_{2}O$	0	ı	-CH2CONHCH2CH2OCH3
1-28	-CH2CH C2H5	6-CH <sub>2</sub> CH <sub>2</sub> OC <sub>12</sub> H <sub>25</sub>	0	ı	-CH2CH2CH2COOH
1-29	-CH2CH C2H5	5-CH <sub>2</sub> CONH-(CH <sub>2</sub> ) <sub>7</sub> OCH <sub>3</sub>	0		-CH2CH2SO2CH3
I-30	-CH2CH C2H5	5-CH <sub>2</sub> CH C <sub>2</sub> H <sub>5</sub>	1	4-NHCOCH <sub>3</sub>	CHO NHCONH— COOH
I-31	-CH2CH C2H5	5 - CH <sub>2</sub> CH $<$ C <sub>2</sub> H <sub>5</sub>	н	4-NHSO2CH3	CONH2
I-32	-CH2CH C2H5	5-CH <sub>2</sub> CH $<$ C <sub>2</sub> H <sub>5</sub>	н	4-c1	-СН2СН2ОН
I-33	- (n) C <sub>6</sub> H <sub>13</sub>	5-(n)C <sub>6</sub> H <sub>13</sub>	0	ŧ	-NHCOCOOC <sub>2</sub> H <sub>5</sub>
I-34	-СН3	$5$ – CH <sub>2</sub> CH $\stackrel{C_6H_{17}}{\subset}$ C <sub>6</sub> H <sub>13</sub>	0	1	-CH2CH2COOC4H9
1-35	-CH2CH C4H9	4 -CH <sub>2</sub> CH $<$ C <sub>2</sub> H <sub>5</sub>	1	5-C4H9(t)	————
I-36	-CH2CH CH3	5-CH <sub>2</sub> CH $<$ C <sub>4</sub> H <sub>9</sub> $<$ C <sub>2</sub> H <sub>5</sub>	0	-	

ж	CH <sub>2</sub> CC <sub>2</sub> H <sub>2S</sub> T CCOH  N N	NHCOCH <sub>2</sub> CH <sub>2</sub> COOH	————инсосн <sub>2</sub> сн <sub>2</sub> соон	-CH2COOC2H5	NO2 CH2OH
R3	1	ı	1	ı	1
п	0	0	0	0	0
R2	5- (n) C4H9	5-CH <sub>2</sub> CH CH <sub>3</sub>	5-CH <sub>2</sub> CH <sub>5</sub>	5-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	6-0CH <sub>2</sub> CH C <sub>4</sub> H <sub>9</sub>
R	-CH2CH_C <sub>6</sub> H <sub>1,7</sub> S- (n) C <sub>4</sub> H <sub>9</sub>	-CH2CH CH3 5	- (n) C <sub>12</sub> H <sub>2</sub> S	- (n) C <sub>12</sub> H <sub>25</sub>	-CH <sub>2</sub> CH C <sub>2</sub> H <sub>5</sub>
Compound		I-38	I-39	I-40	I-41

General Formula (2)

	a	NHCOCH2 CH2 COOH	-CH2CONHCH2CH2OCH3	-CH2COOCH3	-CHCOOH   C12H25	NHCOCH <sub>2</sub> CHCOOH	NHCOCH <sub>2</sub> CH <sub>2</sub> COOH
	చ		-	1	1	ı	,
	E	0	0	0	0	0	0
E(S)	55	GH <sub>3</sub> CH <sub>3</sub> 5	сн, сн, сн, 5-с, сн, сн, сн, сн, сн, сн, сн, сн,	CH3 CH3 5-C-CH2-C-CH3 CH3 CH3	СН3 СН3 5— Ср— СП2— Ср— СН3 СН3 СН3	CH <sub>3</sub> CH <sub>3</sub> 5-c-CH <sub>2</sub> -c-CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub>	CH3 CH3 5CCH2CCH3 CH3 CH3
)— 8 )	ð	- (n) C <sub>8</sub> H <sub>1</sub> 7	- (n) C <sub>8</sub> H <sub>17</sub>	- (n) CgH17	- (n) C <sub>8</sub> H <sub>1</sub> 7	-(n)C <sub>8</sub> H <sub>1</sub> 7	-CH2CH CH3
	Compound No.	11-1	11-2	11-3	11-4	5-II .	9-11

Compound No.	10	23	E	63	٥
11-7	-CH2CH CH3	CH <sub>3</sub> CH <sub>3</sub> 5-C-CH <sub>2</sub> -C-CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub>	0	-	- NHCOCH2CH-COOH CeH17
8-II	-CH2CH CH3	CH3 CH3 5-C-CH2-C-CH3 CH3 CH3	0	-	-сн2соосн3
1I-9	-CH2CH CH3	CH <sub>3</sub> CH <sub>3</sub> 5-C-CH <sub>2</sub> -C-CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub>	0	ı	-сн <sub>2</sub> соон
II-10	-CH2CH CH3	$\begin{array}{cccc} CH_3 & CH_3 \\ 5-C-CH_2-C-CH_3 \\ CH_3 & CH_3 \end{array}$	0	1	-CH2CONHCH2CH2OCH3
II-11	- (n) C <sub>8</sub> H <sub>1</sub> 7	CH <sub>3</sub> 5 – C – CH <sub>2</sub> CH <sub>3</sub> CH <sub>3</sub>	0	1	-CH <sub>2</sub> CH <sub>2</sub> O NHCOCHCH <sub>2</sub> COOH
11-12	- (n) C <sub>8</sub> H <sub>1</sub> 7	CH <sub>3</sub> 5-C-CH <sub>3</sub> CH <sub>3</sub>	0	-	-сн-( сн <sub>2</sub> ) <sub>10</sub> соон Се <sup>н</sup> 13
.II-13	- (n) C12H25	CH <sub>3</sub> 5- ç- CH <sub>3</sub> CH <sub>3</sub>	0	1	-CH <sub>2</sub> CH <sub>2</sub> O
II-14	- (n) C <sub>12</sub> H <sub>25</sub>	сн <sub>3</sub> 5-с-сн2сн3 сн <sub>3</sub>	0	ı	-CH2COOC12H25

Q1 -CH2CH C2H5 -CH2CH C2H5	5- 5- CH <sub>3</sub> F- 7- CH <sub>2</sub> CH <sub>2</sub>	E 0 C	- 5	Q -CH2CH2SO2CH3 -CH5CONHC12H34
1		• •	ı	-NHCOCH2CHCOOH
-CH <sub>2</sub> CH C <sub>6</sub> H <sub>13</sub>	CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub>	0.	1	-CH <sub>2</sub> CH <sub>2</sub> CHC <sub>1,2</sub> H <sub>2</sub> 5       COOH
- (n) C <sub>16</sub> H33	сн <sub>3</sub> 5— с — сн <sub>3</sub> сн <sub>3</sub>	•		-сн <sub>2</sub> сн <sub>2</sub> scнсоон     с <sub>12</sub> н <sub>25</sub>
-CH2CH CH3	CH <sub>3</sub> 5 – C – CH <sub>2</sub> CH <sub>3</sub> CH <sub>3</sub>		, GH3 3-c- CH2CH3 CH3	NHCOCH C <sub>2</sub> H <sub>5</sub>
- (n) C <sub>8</sub> H <sub>17</sub>	CH3 CH3 5-C-CH2-C-CH3 CH3 CH3	•	1	CH <sub>3</sub>
				$\overline{}$

٥	-CH2CH2NHSO2C8H17		NHSO <sub>2</sub> CH <sub>3</sub>	CHO - NHCONH - COOH	COO - COOH	NHCOCH <sub>2</sub> CH <sub>2</sub> COOH	NO <sub>2</sub> CH <sub>2</sub> OH	NHCOCH <sub>2</sub> CH <sub>2</sub> COOH
63	1	1		3-NHCOCH <sub>3</sub>	3-C1	1	1	ı
E	0	0	0	H	н	0	0	0
25	сн <sub>3</sub> 4—с,—сн <sub>3</sub> сн <sub>3</sub>	5-C2H5	3-C <sub>2</sub> H <sub>5</sub>	сн <sub>ј</sub> 5—ç—сн <sub>2</sub> сн <sub>3</sub> сн <sub>3</sub>	с <sup>н</sup> 3 5—ç—ст <sub>2</sub> сн <sub>3</sub> сн <sub>3</sub>	CH <sub>3</sub> CH <sub>3</sub> 5-c-CH <sub>2</sub> -c-CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub>	сн <sub>3</sub> сн <sub>3</sub> 5- ç- сн <sub>2</sub> - сн <sub>3</sub> сн <sub>3</sub> сн <sub>3</sub>	GH <sub>3</sub> GH <sub>3</sub> 5c-CH <sub>2</sub> c-CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub>
10	-(n)C <sub>18</sub> H <sub>3</sub> 7.	-CH <sub>2</sub> CH C <sub>6</sub> H <sub>13</sub>		~ (n) C6H13	- (n) C <sub>6</sub> H <sub>13</sub>	-CH2CH C2H5	-CH2CH C3H5	- (n) C4H9
Compound No.	11-22	11-23	II-24	11-25	11-26	11-27	II-28	11-29

0	-CH2CH2SCH2COOH	-сн <sub>2</sub> сн <sub>2</sub> ссн <sub>2</sub> соон	NHCOCH2CH2COOH	NO <sub>2</sub> — CH <sub>2</sub> OH	NHCOCH2CH2COOH	-СН2СН2SCH2COOH
ρ3	1	ı	ı	ı	ı	1
E	0	. 0	0	0	0	0
. 02	$\begin{array}{cccc} CH_3 & CH_3 \\ 5-C-CH_2-C-CH_3 \\ CH_3 & CH_3 \end{array}$	$c_{H_3}$ $c_{H_3}$ $c_{H_3}$ $c_{H_3}$ $c_{H_3}$	GH <sub>3</sub> 52CH <sub>3</sub> GH <sub>3</sub>	CH <sub>3</sub> CH <sub>3</sub> 5-C-CH <sub>2</sub> -C-CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub>	GH <sub>3</sub> GH <sub>3</sub> 5CCH <sub>2</sub> CCH <sub>3</sub> CH <sub>3</sub> GH <sub>3</sub>	GH <sub>3</sub> GH <sub>3</sub> 5
75	9	-GHGH3	-CH_CH3	-CH C2Hs	-CH C2H5	-CH\ C2H5
Compound No.	II-30	II-31	II-32	II-33	II-34	II-35

<sup>45</sup> Hereinbelow, representative examples represented by the above-mentioned Formulae 6 and A-1 are shown, however, the acope of the present invention shall not be limited by them.

6-1 
$$(t) C_{5}H_{11} \xrightarrow{C_{5}H_{11}(t)} OH \xrightarrow{OH} NHCONH \xrightarrow{CN} CN$$

6-2 
$$(t) C_5 H_{11} - OCHCONH - NHCONH - CN \\ C_6 H_{13} - OCHCONH - CN \\ C_6 H_{13} - CN \\ C_7 H_{13$$

6-3 
$$(t) C_5 H_{11} - OCHCONH - NHCONH - SO_2 C_4 H_5$$

$$C_2 H_5$$

6-4 
$$(t) C_5H_{11} \longrightarrow O_{C_4H_9} O_{NHCONH} \longrightarrow C1$$

6-5 
$$(t) C_9 H_{11} \leftarrow OCHCONH \leftarrow CN$$

$$(t) C_9 H_{11} \leftarrow OCHCONH \leftarrow CN$$

$$CH_{12} \leftarrow CH_{13}$$

6-6

$$(t) C_8 H_{17} \longrightarrow \begin{matrix} C_8 H_{17}(t) \\ OCHCONH \end{matrix} \longrightarrow \begin{matrix} C1 \\ OCHCONH \end{matrix} \longrightarrow \begin{matrix} C1 \\ OCHCONH \end{matrix}$$

15 6-7

6-8

$$(t) C_5 H_{11} - C_5 H_{11}(t) OH NHCONH - CF_3$$

$$(t) C_5 H_{11} - C_4 H_9$$

(t) 
$$C_5H_{11}$$
 OCHCONH NHCONH C1

$$\begin{array}{c|c} C_{10}H_{21} & OH \\ CH_3- & OCHCONH \\ \hline \\ C_2H_5 & \end{array}$$

15 
$$6-12$$
 OH NHCONH NHSO2 OC12H2  $(CH_3)_3$ CCONH

6-13 
$$(t) C_5 H_{11} - C_5 H_{11}(t) \\ C_6 H_{13} - C_6 H_{17}(t)$$

6-14 
$$(t) C_5 H_{11} - C_5 H_{11}(t) OH NHCONH - SO_2 C_4 H_9$$
 
$$C_2 H_5 O CH_3$$

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$$\begin{picture}(20,0) \put(0,0){\line(0,0){0.5}} \put(0,0){\line(0,0){0.5$$

6-16
$$(t) C_5H_{11} \longrightarrow C_5H_{11}(t) \longrightarrow C_6H_{13}$$

$$C_6H_{13} \longrightarrow C_6H_{13}$$

$$C_6H_{13} \longrightarrow C_8H_{11}(t)$$

6-18 
$$(t) C_5 H_{11} - C_5 H_{11}(t) \qquad OH \qquad NHCONH - CN$$
 
$$C_4 H_9 \qquad O \qquad C_5 H_{11}(t)$$

$$_{5}$$
 OH NHCONH SO\_2C\_4H\_9 CL CHCONH OCH\_2CH\_2OH

6-22

6-20 OH NHCONH CN 
$$C_{12}H_{25}$$
 OC $_{4}H_{9}$ 

6-21 
$$(\texttt{t}) \, \texttt{C}_5 \texttt{H}_{11} = (\texttt{t}) \, \text{C}_5 \texttt{H}_{11} \, (\texttt{t}) \qquad \text{OCHCONH} \qquad \text{NHCONH} \qquad \texttt{CN}$$
 
$$\texttt{C}_4 \texttt{H}_9 \qquad \texttt{OCH}_2 \texttt{CH}_2 \texttt{SCH}_2 \texttt{COOH}$$

$$(t) C_5 H_{11} \longrightarrow C_5 H_{11}(t) \qquad OH NHCONH \longrightarrow CN$$

$$C_4 H_9 \qquad OCH_3$$

6-25

6-26

$$(t) \, C_5 H_{11} - \begin{array}{c} C_5 H_{11} \, (t) \\ OCHCONH \\ C_6 H_{13} \end{array} \quad \text{NHSO}_2 CH_3$$

10

5

25

35

..

$$(t) C_{\theta}H_{17} \longrightarrow OCHCONH \longrightarrow OCHCON$$

6-28

$$\begin{array}{c|c} CH_3 & OH \\ C \downarrow C_8H_{17} & OCHCONH \\ \hline \\ C \downarrow H_9 & C1 \\ \end{array}$$

,

6-30 OH OH OH NHCONH SO<sub>2</sub> CH<sub>11</sub>(t) 
$$C_5H_{11}$$
 CH OCHCONH

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$$^{6-31}$$
  $_{\rm C_{12}H_{25}SO_2NH}$  OCH NHCONH SO\_2CH\_3

6-33 
$$C_{5}H_{11}(t)$$
 OH NHCONH—C1  $C_{3}H_{7}(1)$  SCN

6-34 OH NHCONH— SO<sub>2</sub>CH<sub>2</sub>

$$C_{15}H_{31} \quad C_{2}H_{5} \quad O \text{ (CH}_{2})_{3}\text{COOH}$$

6-35 
$$(t) C_0 H_{17} - OCHCONH - SO_2NHCH_3$$

$$C_6 H_{13} F$$

6-37 
$$\begin{array}{c} \text{NHSO}_2\text{CH}_3\\ \text{CN-} \\ \text{CN-} \\ \text{C}_{12}\text{H}_{25} \\ \text{O}\left(\text{CH}_2\right)_2\text{SCHCH}_3\\ \text{COOH} \\ \end{array}$$

$$(\texttt{t}) \, \texttt{C}_{\texttt{S}} \texttt{H}_{\texttt{1}1} - (\texttt{t}) \\ - \texttt{C}_{\texttt{S}} \texttt{H}_{\texttt{1}1} \, (\texttt{t}) \\ - \texttt{C}_{\texttt{H}} \texttt{H} \\ - \texttt{C}_{\texttt{H}} \texttt{H} \\ - \texttt{C}_{\texttt{H}} \texttt{H} \\ - \texttt{C}_{\texttt{H}} \\ - \texttt{C}_{\texttt{$$

$$(\texttt{t}) \texttt{C}_5 \texttt{H}_{11} - (\texttt{t}) \\ - \texttt{OCHCONH} \\ - \texttt{C}_4 \texttt{H}_9 \\ - \texttt{OCH}_2 \texttt{COOCH}_3$$

6-41

$$\begin{array}{c|c} \text{6-42} & \text{OH} & \text{OH} \\ \text{(t)} \text{C}_5\text{H}_{11} & \text{OCHCONH} & \text{NHCONH} \\ \\ \text{C}_2\text{H}_5 & \text{O} \\ \\ \text{OCH}_3 & \text{OCH}_3 \\ \end{array}$$

x:y = 50:50 (weight ratio)

x:y = 50:50 (weight ratio)

As for other specific examples of the pheno-type coupler having a uraicit group, than those given above, for example, those disclosed in Japanese Patent O. P.I. Publication Nos. 56-86 134 (1981), 57-204543 (1982), 57-204543 (1982), 58-3254 (1983), 58-325

$$A-3$$
  $A-4$   $C_{13}H_{27}$   $C_{2}H_{5}$   $C_{2}H_{5}$   $C_{13}H_{27}$   $C_{2}H_{5}$   $C_{4}H_{9}$ 

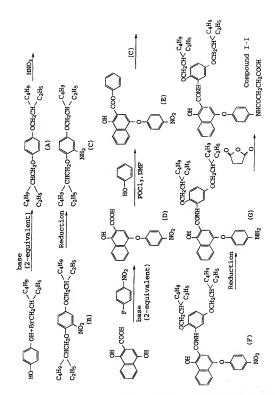
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Herein below, synthetic examples of the cyan dye-forming coupler represented by Formula 1 are given. Synthesis Example 1-1 (Synthesis of Compound I-1)

Compound I-1 can be synthesized according to the following scheme.

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22.g of p-hydroquinone and 77 g of 2-ethylhexyl bromide were dissolved in 150 ml of ethanol. Next, 900 ml of ethanol solution, in which 29 g of potassium hydroxide was dissolved, was added and underwent reaction for ten hours under reflux. After filtrating off the precipitated potassium bromide the solution was condensed and extracted the reaction product by adding ethyl acetate and water, to collect an organic phase. After condensing this 40.5 g of 1,4-di-(2-ethyl-

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hexyloxy/jbenzene(A) in the form of a coloriess oil(), was obtained by vacuum distillation (a temperature range of 200 to 203 °C, a pressure condition is 3 mmHg).

80 ml of chloroform was added to 27 g of (A), and to this 10 g of 65% nitric acid was added dropwise while cooling down the solution at 0 to 3°C. While maintaining cooling, the solution was stirred for one hour and, then, water was added to wash an organic phase. After washing with 5% sodium hydrogencathorate and water, the organic phase was condensed and dried, to obtain 30.6 g of 2,5-di-(2-ethylhexyloxy)nitrobenzene(5) in the form of a yetowish oil. This was used in the next step without refinement.

29 g of (B) was dissolved in 30 ml of methanol and 120 ml of ethyl acetate and, to this 3 g of 5% wat Pol/C catalyst was added to underwent catalytic hydrogenation for ten hours under critinary temperature and critinary pressure. After completion of the reaction, the catalyst was filtered out and, by condensing and dying the filtered solution, 28 g of 2.5 di-(2-ethylhaxyloxy)amiline(C) in the form of a thin-brownish oil was obtained. This was used in the next step without re-insement.

250 g of 1,4-dihydroxy-2-naphthoic acid was added to 1.9 1 of N,N-dimethylformamide and, to this, an aqueous alkaline solution consisting of 103 g of sodium hydroxide and 154 ml of water was added, under introgen gas flow. While maintaining the finer temperature at 30°C, 172 g of 1-fluoro-4-niflobenzene was added taking 10 minutes and stirred for two hours at the inner temperature of 45°C. The mixture was, then poured into 1.8 Kg of locand 250 ml of concentrated hydrochloric acid, and then, solidified crude crystals were filtrated. This was further recrystallized in acetonitrile, to obtain 316 g of 1-hydroxy4-4-nitrophenoxy)-2-naphthoic acid (D) in the form of pale yellowish crystals

250 g of (D) and 87 g of phenol were added to 1.5 liter of chloroform and, then, after 119 g of phesphorous oxychloride was added dropwise, temperature was raised up to reflux temperature and, then under reflux 250 ml of N.N-dimethylormamide was added drowise staling about two hours and the mixture was further stirred for five hours under reflux. After leaving the reaction mixture overnight, it was condensed until the volume of the reaction mixture became about 700 ml and then 21 of methanol was added to this, pracipitated crystal were filtrated to obtain 235 g of 1-hydroxy-4-(Anttocheoxy)2-naphthoic acid phenyl (E) in the form of pale yellowish needle crystals.

21 g of (E) and 20 g of (c) were added to 100 ml of mesitylene and the mixture was stirred for two hours at the inner temperature at 150 to 160°C. After completion of the reaction, white maintaining heating mesitylene and phenol were distilled out under reduced pressure. After coefing down the reaction mixture to 50 to 60°C, 100 ml of 2: 1 mixed solution of aftry a sociate and methanol was added and after cooling with ice, procipitated crystal were filtrated, to obtain 20 g of 1-hydroxy4-cf4-triophenoxy1-N-12,5-di-(2-shitylhoxy1cxy)phnyl/2-sperhalmatic(cf) in the form of pale yellow crystals.

17 g of [7] was dissolved in 170 ml of shipscelete, to this 3 g of 5% wet PdC catalyst was added to undergo catalyst hydrogenation for seven hours under com temperature and atmospheric pressure. After completion of the reaction, the catalyst was filtrated and, by condensing and drying the filtered solution, 16 g of 1-hydroxy-4-(4-aminophenoxy)-N-[25-di-(2-eh/bxy/cay/)phnyl/2-naphthamics(5) was obtained in the form of brownish oil.

4 g of (G) and 0.7 g of succinic acid anhydride were added and dissolved in 40 ml of ethyl acetate, and under reflux the solution was stirred for one hour. After completion of the reaction, water was added and extracted with ethyl acetate and the collected organic phase was conclensed after washing. By refining the crude product was refined by the use of silica oel dromatographyn-haxane-ethyl acetate elutate).

Thus 3.1 g of Compound I-1 was obtained in the form of white crystals.

Result of Elementary Analysis

Formula: C43H54N2O8

20

25

45

50

55

	C(%)	H(%)	N(%)
Calculation:	71.05	7.49	3.85
Experimental	71.02	7.53	3.83

Synthesis Example: 1-2 (Synthesis of Compound I-2)

Compound I-2 can be synthesized according to the following scheme.

Compound I-2

S3 g 1 f.4-di-hydroxy-2-naphthoic acid was dissolved in one liter of N,N-dimethylformamide and thereto an aqueous aliaine solution consisting of 22 g of sodium hydroxide and 33 g of water was added dropviles under Intigeng as flow. After sitting for 30 minutes, a solution consisting of 51 g of N+2-methoxysthylp-2-bromoscetamide and 200 ml of N,N-dimethylformamide ware added dropwise and reacted for four hours under inner temperature condition at 42 to 44°C. Than this was poured into 400 g of lea and 85 m lot water and precipitated crystals were taken by fittration. Further, by recystalizing with acatonitrile, 61 g of 1-hydroxy-4-(2-methoxysthylcarbamoylmethoxy)-2-naphthoic acid(H) was obtained in the form of sela greeniths oction-like crystals.

3 g of (+i) and 3.3 g of (C), which was synthesized in 1-1 above, were dissolved in 70 ml of warmed dioxane and, thereto, a solution consisting of 2.1 g of 1,3-dicyclohacylcarbodimide and 20 ml of dioxane was added. Aglate the solution for one hour under inner temperature at 50°C and, after pracipitated 1,3-dicyclohacylurea by filtration was separated, the filtered solution was condensed. By refilning the obtained reaction mixture by siting agle column chromatography(with n-haxmenethyl acatest by pe aluted, 3 g of Compound 1-2 was obtained in the form of white crystalls.

Result of Elementary Analysis Formula: C<sub>38</sub>H<sub>54</sub>N<sub>2</sub>O<sub>7</sub>

20

50

	C(%)	O(%)	N(%)	
Calculation:	70.13	8.36	4.30	
Eveneriment	70.12	9 90	1 22	

Synthesis examples of the cyan dye-forming coupler represented by Formula 2 of the present invention are illustrated below:

Synthesis Example: 2-1 (Synthesis of Compound II-6)

Compound II-6 can be synthesized according to the following scheme.

20 g of 4-(1,1,3,3-tetramethylbutyl)phenol was dissolved in 100 ml of N,N-dimethylformamide and after 15 g of inches to this, 18 g of polassium carbonatel(%203) was added and stirred for eight hours under inner temperature at 80°C. After completion of the reaction, water was added to the reaction multiure, extracted with eight jeached and the organic phase washed with a saturated aqueous sodium chloride solution. Condensing and drying the product and then by refining it by silica gel column chromatography, to obtain 18 g of 4- isobutyloxy-(1,1,3,3-tetramethylbutyl) benzene ([i) in the form of colorless oil.

8 g of (I) was dissolved in 50 ml Of chloroform and to this 5.5 ml of 61% nitric acid was added dropwise. This was

stirred for two hours under inner temperature at 40°C. After completion of the reaction, water was added to separate the organic phase and washed with water. Condensing and drying the organic phase and, then, by refining it by silica gol column chromatography with n-hexane-ethyl acetate eluate, to obtain 9 g of 2-isobutyloxy-5-(1,1,3,3-tetramethyl-butyl)hirtobergrane (J) in the form of yellowish oil.

8 g of (J) was dissolved in 50 ml of methanol and , to this, 1 g of 5% wet Pd/C catalyst was added, to undergo contact hydrogenation for three hours under room temperature and atmosheric pressure. After completion of the reaction, the catalyst was filtrated out and the filtered solution was condensed and dried to obtain 7 g of 2-isobutyloxy-5-(1,1,3,3-4e-tramethylbutylsailine (K) in the form of brownish oil.

4 g of (E)(cf. Synthesis Example I-1) and 3 g of (K) were added into 20 ml of mesitylene and this was stirred for three hours under inner temperature at 150 to 160°C. After completion of the reaction and, while keeping heating, mesitylene and phenol were distilled off. After cooling down the reaction mixture to 5°C o6°C, 30 ml of 21 mixed solvent of ethyl acetate and methanol was added. After cooling down the reaction mixture with ice, precipitated crystals were filtered and 4.8 g of 1-yidroxy -4(4-nitrophenoxy)-N-[2-isobutyloxy-5-(1,1.3,3-tetrametrylbutyl)phenyl}-2-naphthamide (L) was obtained in the form of pale yellowish roystals.

4 g of (L) was dissolved in 50 ml of ethyl acetate and, to his, 0.5 g of 5% wet PdC catalyst was added, to undergo contact hydrogenation for eight hours under room temperature and atmospheric pressure. After completion of the reaction the catalyst was filtrated out and the filtered solution was condensed and dried to obtain 3.5 g of 1 hydroxy-4-(4-aminophenoxy)-N-[2-isobutyloxy-5-(1,1,3,3-tetramethylbutyl)phenyl)-2-naphthoamide (M) in the form of paile brownish solid.

3 g of (M) and 0.6 g of succinic acid anhydride were added to 30 ml of ethyl acetate and stirred under reflux for one and half hours. After completion of the reaction water was added and extracted with ethyl acetate. After washing with water the collected organic phase was condensed by refining the crude product, by silice gel column chromatography with n-hexane-ethyl acetate bype eluste, 2.1 g Compound II-6 was obtained in the form of white crystals.

Result of Elementary Analysis:

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Chemical Formula: C39H4EN2O7

	C(%)	H (%)	N(%)
Calculation:	71.54	7.08	4.28
Experiment:	71.51	7.10	4.27

Synthesis Example 2-2(Synthesis of Compound II-10)

Compound II-10 is synthesized according to the following scheme.

$$(H) \xrightarrow{\text{CK}} \begin{array}{c} \text{OH} \\ \text{CONH} \\ \text{CH}_3 \\ \text{CH}_3$$

Compound II-10

3 g of (+) and 2.7 g of (K)(cf. Synthesis Example 2-1 above) were dissolved in 70 ml of dioxane and, to this, 2.1 g of 1,3-dicyclohexylearbodilmide and 20 ml of dioxane were added. The solution was stirred at inner temperature of 50 °C for one and a half hours. After filtrating of the precipitated 1,3-dicyclohexylures, the resection mixture solution was filtered and the littered solution was condensed, and the crude product was obtained. The crude product was refined by silics gel column chromatography with n-hexaneethyl acetate type eluate, 3.2 g of Compound II-10 was obtained in the form of white crystals.

Result of Elementary Analysis: Chemical Formula: C<sub>34</sub>H<sub>46</sub>N<sub>2</sub>O<sub>6</sub>

	C(%)	H (%)	N(%)
Calculation:	70.56	8.01	4.84
Experiment:	70.54	8.04	4.83

In the present invention, the cyan dye-forming coupler represented by the above-mentioned Formula 1 or 2 is incorporated in at least one red-sensitive silver halide emulsion layer.

The cyan dye-forming couplers represented by the formulae 1 and 6 or formulae 2 and 6 can be used in the optional proportion, however, preferably, within a molar ratio of 1/1 to 1/10. The cyan dye-forming couplers represented by the Formulae 1, 2 and 6 may be used in the quantity of 1x10<sup>-3</sup> to 8x10<sup>-1</sup> mol and, more preferably, 1x10<sup>-2</sup> to 8x10<sup>-1</sup> mol per a mol of sliver halide.

Amount of the compound represented by the Formula A-1 is preferably 0.01 to 10 g and, more preferably, 0.1 to 3.0 g per one gram of the cyan dye-forming coupler represented by Formulas 1, 2 or 6. Moreover the compound represented by the Formula A-1 may be used either one kind or two or more kinds in combination.

In order to incorporate compound represented by Formulas 1, 2, 6 or A-1 used in the present invention in a silver haide emulsion layer, it is possible to apply a method, in which the above-mentioned compound or compoundes are first dissolved in a conventionally known high boiling-point solvent, such as dibutyl prihaiate, tricreey phosphate or combination of the high boiling-point solvent and a low boiling-point solvent such as butyl scetate, either singly or in combination, respectively. Then the coupler solution is mixed with an aqueous solution containing geliating and a surface active agent. Subsequently, after the solution is subject to emulsification, using a high-speed rotary mixer, such as a colloid mill or a ultra-sonic homogenizer, this may be incorporated into the emulsion, either directly or after it being is set, our and washed with water.

The compound represented by Formulas 1, 2, 6 or A-1 may be incorporated in the silver halide emulsion layer either separately after separately dissolving in the high boiling-point solvent and dispersing in the above-mentioned method, or at a line. Furthermore, concerning the compounds represented by Formulas 1, 2, 6 or A-1 it is preferable that compounds are dissolved, and dispersed altogether and incorporated in the silver halide emulsion layer.

As for sliver halide emulsion used in the light-sensitive material of the present invention, any kind of sliver halide emulsion which is known in the art can optionally be employed.

The emulsion may undergo a conventional chemical sensitization, and can be spectrally sensitized with a conventional sensitizing dye, to make the emulsion sensitive to any pre-designed spectral region.

The sliver halide emulsion can comprise one or more kinds of photographic additives such as an anti-foggant, a stabilizer, etc. As for the binder for the emulsion, it is preferable to use gelatin.

The silver halide emulsion layer and other hydrophilic colloidal layer may be hardened and can comprise a plasticizer and dispersion containing a polymer which is insoluble or sparsely soluble in water. A coupler is used in the silver halide emulsion layer of the color photographic light-sensitive material.

It is also possible to use a colored coupler having a function as a color compensator, a competing coupler, a compound which is, upon reaction with an exidation product of a color developing agent capable of splitting of a pridographically useful fragment such as a development accelerator, a bleach accelerator, a developing agent, a solvent for the silver halide, a color toning agent, a hardener, a fogging agent, an anti-foggant, a chemical sensitizer, a spectral sensitizer, a desensitizing accent.

As for the support, for example, paper laminated with a polymer such as polyethylene, a polyethyleneterephthalate film, a baryta paper and a cellullose triacetate may be used.

In order to obtain a dye image using the light-sensitive material of the present invention, color photographic process which is generally known in the art may be applied.

The present invention can be applied to any type of silver halide light-sensitive materials known in the art, including negative-type color films, color papers and reversal-type color films.

## Examples

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Hereinbelow the present invention is further explained with reference to working examples, however, the scope of the present invention is not limited by them.

In all of the following examples, the amount of addition of the additive in the sliver halide light-sensitive photographic material is given, unless defined otherwise, in terms of weight (g) a square meter of the light-sensitive material. Concerning the amount of sliver halide and colloids liver, they are expressed in terms of equivalent amount of sliver.

## EP 0 690 344 A1

# Example 1

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On a triacetylcellullose film support, respective layers, the components of which are given below, are provided in order to prepare a multi-layer silver halide light-sensitive color photographic material (Sample No.1).

First Layer: Anti-Halation Layer (HC-1)

Black colloidal silver	0.20
UV Absorbent (UV-1)	0.20
Colored coupler (CC-1)	0.05
Colored coupler (CM-1)	0.05
High boiling-point solvent (Oil-1)	0.20
Gelatin	1.5

Second Layer: Intermediate Layer (IL-1)

UV absorbent (UV-1)	0.01
High boiling-point solvent (Oil-1)	0.01
Gelatin	1.5

Third Layer: Low red light-sensitive silver halide emulsion layer (RL)

	Silver iodobromide emulsion (Em-1)	0.8		
0	Silver iodobromide emulsion (Em-2)	0.8		
	Sensitizing dye (SD-1) $2.5 \times 10^{-4}$ mols a mo	ol of silver		
5	Sensitizing dye (SD-2) $2.5 \times 10^{-4}$ mols a mo	ol of silver		
	Sensitizing dye (SD-3) $0.5 \times 10^{-4}$ mols a mo	ol of silver		
	Cyan dye-forming coupler (C-A)	1.0		
10	Colored cyan coupler (CC-1)	0.05		
	DIR compound (D-1)	0.002		
45	High boiling-point organic solvent (0i1-1)			
		0.5		
	Gelatin	1,.5		

# Fourth Layer: High red light-sensitive silver halide emulsion layer (RH)

5	Silver iodobromide emulsion (Em-3)	2.0		
•	Sensitizing dye (SD-1) $2.0 \times 10^{-4}$ mols a m	ol of silver		
	Sensitizing dye (SD-2) 2.0x10 <sup>-4</sup> mols a m	ol of silver		
10	Sensitizing dye (SD-3) $0.1 \times 10^{-4}$ mols a m	ol of silver		
	Cyan dye-forming coupler (C-A)	0.25		
15	Cyan dye-forming coupler (C-B)	0.05		
	Colored cyan coupler (CC-1)	0.015		
	DIR compound (D-1)	0.05		
20	High boiling-point organic solvent (Oil-	1)		
		0.2		
25	Gelatin	1.5		

Fifth Layer: Intermediate Layer (IL-2)

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Gelatin 0.5

# Sixth Layer: Low green light-sensitive silver halide emulsion layer (GL)

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	Silver iodobromide emulsion (Em-1) 1.3
	Sensitizing Dye (SD-4) $5 \times 10^{-4}$ mols a mol of silver
40	Sensitizing dye (SD-5) $1 \times 10^{-4}$ mols a mol of silver
	Magenta dye-forming coupler (M-1) 0.25
45	Magenta dye-forming coupler (M-2) 0.25
	Colored magenta coupler (CM-1) 0.01
	DIR Compound (D-3) 0.02
50	DTR Compound (D-4) 0.020

	High boiling-point organic solvent (0i1-2)
5	0.3
	Gelatin 1.0
10	Seventh Layer: High green light-sensitive silver halide emulsion layer (GH)
	Silver iodobromide emulsion (Em-3) 1.3
15	Sensitizing Dye (SD-6) 1.5x10-4 mols a mol of silve
	Sensitizing dye (SD-7) 2.5x10-4 mols a mol of silve
20	Sensitizing dye (SD-8) $0.5 \times 10^{-4}$ mols a mol of silve
	Magenta dye-forming coupler (M-1) 0.05
	Magenta dye-forming coupler (M-2) 0.10
25	Colored magenta coupler (CM-2) 0.05
	DIR Compound (D-3) 0.01
30	High boiling-point organic solvent (0i1-2)
	0.2
	Gelatin 1.0
35	Eighth Layer: Yellow Filter Layer (YC)
40	Yellow collected sliver Anti-dye staining agent (SC-1) High boiling-point organic solvent (Cli-5) Gelatin 0.8
45	Ninth Layer: Low blue light-sensitive silver hallde emulsion layer (BL)
	Silver iodobromide emulsion (Em-1) 0.25
50	Silver iodobromide emulsion (Em-2) 0.25

Sensitizing dye (SD-10)

	$7 \times 10^{-4}$ mols a mol of silver	
5	Yellow dye-forming coupler (Y-1) 0.5	
	Yellow dye-forming coupler (Y-2) 0.1	
10	DIR Compound (D-2) 0.01	
	High boiling-point organic solvent (0i1-2)	
	0.3	
15	Gelatin 1.0	
	Tenth Layer: High blue light-sensitive silver halide emulsion layer (BH)	
20	Silver iodobromide emulsion (Em-4) 0.4	
	Silver iodobromide emulsion (Em-1) 0.4	
25	Sensitizing dye (SD-9) $1 \times 10^{-4}$ mols a mol of silver	
	Sensitizing dye (SD-10)	
	$3x10^{-4}$ mols a mol of silver	
30	Yellow dye-forming coupler (Y-1) 0.30	
	Yellow dye-forming coupler (Y-2) 0.05	
35	High boiling-point organic solvent (Oil-2)	
	0.15	
40	Gelatin 1.1	
~	Eleventh Layer: First protective layer (PRO-1)	
	Fine grain silver iodobromide emulsion	
45	(Average grain size: 0.08 µm; AgI content: 2 mol%)	
	0.4	
50	UV Absorbent (UV-1) 0.10	
	UV Absorbent (UV-2) 0.05	

High boiling-point organic solvent (Oil-1)

High boiling-point organic solvent (0i1-3)

			0.1
Formalin	scavenger	(HS-1)	0.5
Formalin	scavenger	(HS-2)	0.2

Gelatin 1.0

Twelfth Layer: Second Protective Layer (PRO-2)

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Surface active agent (Su-1)	0.005	
Alkali-soluble matting agent (Average grain size: 2 µm)	0.05	
Polymethylmethacrylate (Average grain diameter: 3 µm)	0.05	
Lubricant (WAX-1)	0.04	
Gelatin	0.6	

Respective layers contain, in addition to those components mentioned above, a coating aid Su-2, a dispersion aid Su-3, gelatin hardeners H-1 and H-2, and anti loggents AF-1 and AF-2.

Sliver halide emulsions used in this example are as follows.

Em-1: an emulsion containing core/shell-type mono-disperse silver halide grains, of which average grain size, average silver iodide content and dispersion of width are  $0.46\,\mu m$ , 7.0 mol% and 14%, respectively.

Em-2: an emulsion containing core/shell-type mono-disperse silver halide grains, of which average grain size, average silver lodicle content and dispersion of width are 0.30 μm, 2.0 mol% and 14%, respectively.

Em-3: an emulsion containing core/shell-type mono-disperse silver halide grains, of which average grain size, average silver iodide content and dispersion of width are 0.81 µm, 7.0 mol% and 14%, respectively.

Em-4; an emulsion containing core/shell-type mono-disperse silver hallde grains, of which average grain size, average silver lodide content and dispersion of width are 0.95 µm, 8.0 mo/% and 14%, respectively.

In the above, distribution of width is expressed in the following equation:

Distribution of width(%) = (standard devlation/average grain size) x 100

SD-2

SD-5 
$$C_2H_5$$
  $C_2H_5$   $C_2H_$ 

SD-6 
$$C_2H_5$$
  $C_2H_5$   $C_2H_$ 

SD-7

SD-8

$$\bigcap_{\substack{\text{O} \\ \text{N} \\ (\text{CH}_2)_4\text{SO}_3}^{\text{C}_2\text{H}_5}} \bigcap_{\substack{\text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5}} \bigcap_{\substack{\text{C}_2\text{H}_5 \\ \text{C}_2\text{$$

SD-9

SD-10 
$$CH_{3}O$$
  $CH$   $CH_{2})_{3}SO_{3}^{-}$   $CH$   $CH_{2})_{3}SO_{3}^{-}$   $(CH_{2})_{3}SO_{3}^{-}$   $(CH_{2})_{3}SO_{3}^{-}$ 

C-B (Comparative Coupler)  $C_5H_{11}(t)$ 10 OCH2CONHCH2CH2OCH3 RC-1 (Comparative Coupler) 15 20 RC-2 (Comparative Coupler) 25 RC-3 (Comparative Coupler) 35

$$\begin{array}{c} \text{NHCO-} \\ \text{N} \\ \text{NHSO}_2 \\ \text{C1} \\ \text{C1} \\ \text{C1} \end{array}$$

Y-1

$$\begin{array}{c|c} & \text{C1} \\ \text{CH}_3\text{O} & \begin{array}{c} \text{COCHCONH} \\ \\ \text{O} & \begin{array}{c} \text{N} \\ \\ \text{N} \\ \end{array} \end{array} \begin{array}{c} \text{COCC}_{12}\text{H}_{25} \end{array}$$

Y-2

$$\begin{array}{c} \text{C1} \\ \text{(CH}_3)_3\text{CCOCHCONH} \\ \text{O} \\ \text{N} \\ \text{O} \\ \text{N} \\ \text{-N} \\ \text{-N} \\ \text{-CH}_2 \\ \text{---} \end{array}$$

CC-1

CM-2

D-1

$$\begin{array}{c|c} OH & \\ OC_{1}H_{2}S \\ \hline \\ N & \\ N & \\ N & \\ CH_{3} & \\ \end{array}$$

$$\begin{array}{c} \text{OH} \\ \text{CONH-} \\ \text{OC}_{14}\text{H}_{29} \\ \text{CH}_{2}\text{S-} \\ \text{N-N} \\ \text{N-N} \end{array}$$

D-3

D-4

Su-3 SC-1 OH 
$$C_{18}H_{37}$$
 (sec)  $C_{13}H_{25}$ 

$$\begin{array}{c|c} \text{WAX-1} & & \text{CH}_3 & \text{CH}_3 \\ \text{CH}_3 - \text{Si-O} & \text{Si-O} & \text{Si-CH}_3 \\ \text{CH}_3 & & \text{CH}_3 & \text{CH}_3 \end{array}$$

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Next, in Sample No.1 above, cyan dye-forming couplers C-A and C-B, which are incorporated in the third and the fourth silver halide emulsion layers, were replaced by equivalent moits around of Comparative couplers RC-1, RC-2 and RC-3 and the cyan dye-forming couplers according to the present invention as shown in Tables 1.

Thus prepared samples were subjected to exposure with white light for 1/100 second through an optical wedge and, thereafter processed according to "Processing A" and "Processing B"

# Processing Steps (at 38°C)

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Processing Step Time Color Development 3'15" 6'30" Bleaching Washing 3'15" Fixing 6'30" Washing 3'15" Stabilizing 1'30" Drying

Ingredients of the processing solutions used in the respective processes are as follows; provided that in "Processing A', "Bleaching Solution A" and in "Processing B", "Bleaching Solution B" were used, respectively.

<Color Developing Solution>

4-Amino-3-methyl-N-ethyl-N-(β-hydroxyethyl) -

25	aniline sulfate	4.75 g
20	Sodium sulfite unhydride	4.25 g
30	Hydroxylamine 1/2 sulfate	2.0 g
	potassium carbonate unhydride	37.5
	Sodium bromide	1.3 g
35	Tri-sodium nitrilo-triacetate monohydrate	2.5 g
	Potassium hydroxide	1.0 g

Add water to make the total volume 1 liter and adjusted pH at 10.2 with ammonia water.

# <Bleaching Solution A>

Ammonium ferric(III) ethylenediaminetetracetic acid	100 g
Diammonium ethylenediaminetetracetic acid	10.0 g
Ammonium bromide	150.0 g
Acetic acid	10 ml

Add water to make the total volume 1 liter and adjusted pH of the solution at 6.0 with ammonia water.

## <Bleaching Solution B>

This solution has the same composition as "Bleach Solution A" except that 2.5 g of sodium hydrosulfite was added to a liter of the above-mentioned "Bleaching Solution A".

<Fixing Solution>

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Ammonium thiosulfate	175.0 g
Anhydrous sodium sulfite	8.5 g
Sodium metasulfite	2.3 g

Add water to make the total volume one liter and adjusted pH of the solution at 6.0 with acetic acid

<Stabilizing Solution>

Formalin(37% aqueous solution)	1.5 ml	١
Konidax(a product of Konica Corporation)	7.5 ml	

Add water to make the total volume one liter.

With respect to the thus obtained by e images produced in Samples 1 through 30 according to the above-mentioned color developing steps, sensitivities of the red-sensitive layer of the Samples were measured using an optical densitivate type PD-8-5, a product of Konica Corporation. The sensitivity was obtained in terms of a reciprocal of exposure necessary to give the minimum density plus 0.1 and expressed as relative values as shown in Table 1, in which sensitivity of Sample 1 was normalized as 100.

The term "maximum absorption" means the maximum absorption wavelength(nm) of a sample at a portion of which density measured with red light is 1.0, when it is processed with "processing A".

The term "density difference" in Tables 1 and 2 represents numeral values of the 100-times-multiplied ratio of the maximum densities of the respective samples measured with red light between when it is processed with "processing A" and "Processing B".

The term "storage preservation property before exposure" represents density differences in the fog in the red-sensitive layer of the samples, one of which is placed under atomospheric conditions at 55°C and 65% R.H. for three days and, thereafter subjected to exposure and developing process with "Processing A" and another which does not undergo such experiment.

Results are shown in Table 1 and Table 2.

Table 1

δ	Sample No.	C-A Substi- tution	C-B Substi- tution	Relative Sensi- tivity	Maximum Absorp- tion	Density Differ- ence	Storage Preservation property before Exposure	Remarks
	1	C-A	C-B	100	697	63	0.13	Comp.
10	2	RC-1	RC-2	89	637	93	0.11	Comp.
	3	RC-3	RC-3	85	701	95	0.09	Comp.
	4	RC-3	RC-2	91	702	94	0.10	Compo.
	5	RC-3	I-1	110	700	96	0.09	Inv.
15	6	RC-3	I-2	107	700	96	0.08	Inv.
	7	I-3	RC-2	106	699	96	0.08	Inv.
	8	I-1	I-1	125	698	98	0.07	Inv.
	9	I-2	I-1	123	697	99	0.07	Inv.
20	10	1-2	I-2	116	698	99	0.05	Inv.
	11	I-2	I-4	115	698	98	0.06	Inv.
	12	I-2	I-6	124	697	98	0.07	Inv.
	13	I-3	I-1	120	697	99	0.07	Inv.
25	14	I-3	I-2	115	698	98	0.06	Inv.
	15	I-3	I-5	119	698	98	0.06	Inv.
	16	I-3	I-14	122	697	98	0.06	Inv.
	17	I-4	I-1	124	697	98	0.07	Inv.
30	18	I-4	I-6	123	697	99	0.07	Inv.
	19	I-4	1-7	120	698	98	0.07	Inv.
	20	I-4	I-12	122	698	98	0.07	Inv.
	21	I-19	1-8	117	698	98	0.07	Inv.
35	22	I-22	I-1	114	698	97	0.07	Inv.
	23	I-33	I-2	112	698	96	0.08	Inv.
	24	I-37	I-1	113	699	96	0.08	Inv.

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Table 2

Sample No.	C-A Substi- tution	C-B Substi- tution	Relative Sensi- tivity	Maximum Absorp- tion	Density Differ- ence	Storage Preservation property before Exposure	Remarks
1	C-A	С-В	100	697	63	0.13	Comp.
2	RC-1	RC-2	89	637	93	0.11	Comp.
3	RC-3	RC-3	85	701	95	0.09	Comp.
4	RC-3	RC-2	91	702	94	0.10	Comp.
25	RC-3	II-1	110	699	95	0.09	Inv.
26	RC-3	II-2	106	700	95	0.09	Inv.
27	II-10	RC-2	107	699	95	0.08	Inv.
28	II-1	II-1	126	697	97	0.07	Inv.
29	II-2	II-1	125	696	98	0.06	Inv.
30	II-2	II-2	115	697	97	0.06	Inv.
31	II-2	II-4	120	697	97	0.07	Inv.
32	II-2	II-6	125	697	98	0.07	Inv.
33	II-3	II-1	120	697	97	0.07	Inv.
34	TI-3	II-5	126	696	97	0.07	Inv.
35	II-3	II-11	124	697	97	0.06	Inv.
36	II-3	II-19	122	696	97	0.07	Inv.
37	II-10	II-1	120	697	97	0.07	Inv.
38	II-10	II-2	116	698	98	0.07	Inv.
39	II-14	II-6	119	697	97	0.07	Inv.
40	II-14	II-10	115	697	97	0.07	Inv.
41	II-15	II-1	118	698	97	0.07	Inv.
42	II-15	11-12	117	698	96	0.07	Inv.
43	II-24	II-1	111	699	96	0.08	Inv.
44	II-25	II-1	113	699	96	0.07	Inv.

As obvious from Tables 1 and 2, it is understood that the samples containing the cyan dye-forming coupler according to the present invention have enhanced sensitivity, tavorable maximum absorption wavelength, reduced density difference even when it is processed with a fatigue bleaching solution and improved storage preservation property before exposure.

## Example 2

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Sample 2-1 was prepared in the same manner as in Sample 1 of Example 1, except for the following items 1 through

Item 1: 1.0 (g) of Cyan dye forming coupler (C-A) employed in 3rd layer of Sample 1 is replaced with 0.7 (g) of Cyan dye forming coupler (C-B).

Item 2: 0.25 (g) of Cyan dye forming coupler (C-A) and 0.05 (g) of Cyan dye forming coupler (C-B) employed in Sample 1 were replaced with 0.20 of Cyan dye forming coupler (C-B).

Item 3: DIR compound (D-2) employed in 9th layer of Sample 1 was replaced with DIR compound (D-2A).

Samples 2-2 through 2-5 were prepared in the same manner as in Sample 2-1, except that the coupler C-B amployed in 3rd and thi layers of Sample 1 was replaced with the same mole of the coupler shown in Table 3, respectively. The above-mentioned Samples 2-1 through 2-5 were evaluated by the same method disclosed on pages 51 and 52.

Table 3

Sam- ple	Cyan Dye-F Coupl		High Boiling-	Rela- tive	Den- sity	λmax at	Storage Preser-	Re- marks
No.	No.	Molar Ratio	Point Solvent	Sensi- tivity (%)	Change (%)	Dred = 2.0	vation Property, ΔFog	
2-1	C-B	1	oil-1	100	53	697	0.11	Comp.
2-2	I-1/6-22	0.5/0.5	oil-1	184	97	696	0.07	Inv.
2-3	II-34/6-40	0.5/0.5	oil-1	183	97	696	0.06	Inv.
2-4	T-1	1	A-1	184	96	697	0.06	Inv.
2-5		ī	A-7	183	96	697	0.06	Inv.

As obvious from the results shown in Table 3, it is understood that Samples No.2-2 through 2-5, which are according to the present invention, have enhanced sensitivity, excellent processing stability without shift of the absorption wave-length in the high density portion of the image and improved storage preservation properly before exposure.

On the other hand, Comparative Sample 2-1, in which Comparative dye-forming coupler C-B and high boiling-point solvent DI-1 are used, have good optical absorption, however, density change in the processing with the fatigue bleaching solution and fogging in the storage before exposure are large.

#### Claims

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 A silver halide color photographic light-sensitive material comprising a support and provided thereon, a blue-sensitive silver halide omulsion layer, a green-sensitive silver halide emulsion layer and a red-sensitive silver halide emulsion layer, wherein said red-sensitive silver halide emulsion layer comprises a compound represented by Formula 1 or Formula 2:

Formula 1

wherein  $\mathbb{H}_1$  and  $\mathbb{H}_2$  independently represent an aliphatic group, provided that the total number of carbon atoms contained in  $\mathbb{H}_1$ , and  $\mathbb{H}_2$  is 8 or more,  $\mathbb{H}_3$  represents a substituent;  $\mathbb{H}_1$  is 0 or 1 and  $\mathbb{H}_2$  represents an aliphatic group, an any group or a heterocyclic group;

Formula 2

$$OH \longrightarrow OQ_1$$

$$(Q_3)_m$$

wherein  $\Omega_1$  and  $\Omega_2$  independently represent an aliphatic group, provided that the total number of carbon atoms considered in  $\Omega_1$  and  $\Omega_2$  is 8 or more;  $\Omega_2$  appresents a substituent; m represents  $\Omega$  or 1;  $\Omega$  represents an aliphatic group, an any force or a feature of the considered group, an any force or a feature of the considered group.

The silver halide color photographic light-sensitive material of claim 1, wherein said red-sensitive silver halide emulsion layer further comprises a compound represented by Formula 6:

## Formula 6

$$\begin{array}{c} \text{OH} \\ \text{NHCONHR}_{11} \\ \\ \text{R}_{12}\text{CONH} \\ \\ \text{X}_{11} \end{array}$$

wherein R<sub>11</sub> represents an anyl group or a heterocyclic group; R<sub>12</sub> opresents an allyl group or an anyl group, provided that R<sub>12</sub> may form a group capable of forming a dimer or an oligomer with R<sub>11</sub> or R<sub>12</sub>; X<sub>11</sub> represents a hydrogen atom or a group capable of splitting off upon reaction with an oxidation product of a color devolciping agent.

The silver halide color photographic light-sensitive material of claim 1, wherein said red-sensitive silver halide emulsion layer further comprises a compound represented by Formula A-1:

## Formula A-1

wherein R<sub>21</sub>, R<sub>22</sub> and R<sub>23</sub> independently represent a hydrogen atom, an alkyl group, a cycloalkyl group or an arvi group.

The silver halide color photographic light-sensitive material of claim 1, wherein said -O-Q of said Formula 2 represents an aliphaticoxy group, a heterocyclicoxy group or a

wherein R<sub>A</sub> represents an alkyl group, a nitro group, an amino group, an alkoxyl group, a hydroxyalkyl group, a carbarnoyl group, a carbarnoyl group, a carbarnoyl group, an alkoxyl group, a carbarnoyl group, an alkoxyl group, an alkoxyl group, an alkoxycarbonyl group, an alkoxyl group, an alkoxyl group, an alkoxycarbonyl group, an alkoxyl group, an alkoxyl group, an alkoxycarbonyl group, an alkylamino group, an arylamino group, an alkoxycarbonyl group, an alkylamino group, an arylamino group, an alkoxycarbonyl group, an alkoxylamino group, an anylamino group, an anylamino group, an alkoxybarbonyl group, an alkoxy

50 5. The silver halide color photographic light-sensitive material of claim 1, wherein the compound represented by said Formula 1 is represented by Formula 3:

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## Formula 3

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wherein R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub> and R<sub>7</sub> independently represent a straight-chained or branched alkyl group, provided that the contraction of the contraction atoms contained in R<sub>4</sub> through R<sub>7</sub> is 6 through 25, Pr propsesants a substituted alkyl group having 2 to 30 carbon atoms as a substituted annyl group having 6 to 30 carbon atoms.

The silver halide color photographic light-sensitive material of claim 1, wherein the compound represented by Formula 2 is represented by Formula 4:

## Formula 4

wherein Q<sub>4</sub> represents a straight-chain, branched or cyclic alkyl group; Q<sub>5</sub> represents a tertiary alkyl group having 4 to 20 carbon atoms or a live member or six-member cyclic alkyl group; Q<sup>2</sup> represents a substituted alkyl croup having 2 to 30 carbon atoms or a substituted phenyl group having 6 to 30 carbon atoms.

The silver halide color photographic light-sensitive material of claim 6, wherein said -O-Q' of said Formula 4 represents an aliphaticoxy group, a heterocyclicoxy group or a

- The silver halide color photographic light-sensitive material of claim 2, wherein the compound represented by Formula 1 or Formula 2 and the compound represented by Formula 6 are contained in a molar ratio of 1:1 to 1:10.
  - The silver halide color photographic light-sensitive material of claim 1, wherein said compound represented by Formula 1 or Formula 2 is contained in an amount of 1 × 10<sup>-3</sup> mol to 8 × 10<sup>-1</sup>mol per mol of silver halide.
  - 10. The silver halide color photographic light-sensitive material of claim 1, wherein said compound represented by Formula 1 or Formula 2 is contained in an amount of 1 × 10<sup>-2</sup> mol to 8 × 10<sup>-1</sup> mol per mol of silver halide.



European Patent

# EUROPEAN SEARCH REPORT

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